

JOINT SYMPOSIUM ON OIL SHALE, TAR SANDS, AND RELATED MATERIAL
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HOT WATER PROCESSING OF ATHABASCA OIL SANDS:
I. OIL FLOTATION IN A STIRRED REACTOR

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The laboratory separation of bitumen from Athabasca oil tar sands in hot water, was reported by Clark and Pasternak nearly four decades ago (1). The apparatus was large, requiring 17 pounds of tar sands per run. Later modifications required batches of 6.5 kilograms of sand (2,3,4). Even with the large size, these devices were able to separate only 75-85% of the bitumen from the good tar sands and less than 50% from sands containing higher amounts of clay. In order to recover more oil, the suspension of clay in water has to be passed into an air flotation cell (5).

A very simple technique was also employed by Clark and coworkers for demonstration purposes (6). As we used it, the method is to hand-stir the sands-water mixture (pulp) in a beaker over a steam bath and to add this pulp with agitation into hot water at 85°C. After the stirrer is stopped, the oil froth which rises to the surface is scraped off. This method can give good froth yields from choice samples of oil sands (14-16% bitumen) but the yields drop to 30-50% from ordinary "good" grade sands (10-12% bitumen). From sands containing high amounts of fines (mineral <325 microns in size) yields drop to 10% or less of the bitumen recovered as froth.

In order to investigate the chemistry of the hot water separation, we needed a laboratory technique which would give high yields from a wide range of tar sands and preferably from small samples. Also, the method should be as simple as possible to enable us to arrive at an unequivocal explanation of the phenomenon. The key to such a method proved to be proper agitation of the pulp, the tar sands-water mixture containing about 20% water.

EXPERIMENTAL

The reactor was an electrically heated steel reactor, cylindrical with a round bottom, 3-1/8" inside diameter. The U-shaped impeller 2-5/8" diameter, 1/4" wide, and 1-1/2" high was positioned at the bottom of the reactor to give 1/4" clearance from the wall of the reactor. For speeds up to 350 rpm, the agitator was driven by a laboratory electronic stirrer motor through chain-and-sprocket linkage. At higher speeds a direct drive through a Jacobs chuck was used. The temperature of the reactor was controlled at 85°C. automatically and monitored continuously by thermocouples.

In the normal procedure, 200 grams of tar sand were put into the heated reactor and the top bolted on. Hot water, enough to give a pulp containing 80% tar sand (dry basis) was then forced into the reactor. Enough sodium hydroxide was dissolved in the water to give a pulp having a pH of 8.2. After the material was stirred for 20 minutes, water at 85°C. was introduced to dilute down to 35% tar sand. The agitation was continued at about 50 rpm for ten minutes after which the reactor was disassembled and the froth scraped with a spatula. The watery layer was removed with suction and the sand tailings were scooped out. All fractions were weighed.

The fractions were extracted with a 4:1 mixture of benzene and methylethylbutene. Water was removed simultaneously by the Dean Stark technique. The extraction thimble was dried and weighed to calculate the mineral. To obtain the weight bitumen, the solvents were stripped from the extract. Water was determined by difference. The starting tar sand was similarly analyzed.

All samples of tar sands were homogenized by forcing the sands through 1/4" screen. To slow down their aging (6), the sands were refrigerated until used.

RESULTS

pH

The first variable studied was the effect of pH on yield of froth from high-clay tar sands.

The data in Table show a maximum in yield around pH 8.2, similar to that found in the pilot plant (5). As clay content increases, the yield becomes more sensitive to pH. Also, increasing the clay decreases the oil yield from these sands conditioned at 350 rpm.

Table I

Effect of pH on Oil Yield					
Pulp conditioned at 350 rpm					
Tar Sand	% Bit.	NaOH meq/100 gm. sands	pH	Yield % Bit.	% Mineral in Dry Oil
A	8.0	.31	7.6	39	14
		.62	8.1	68	12
		.94	8.2	72	12
		1.25	8.7	68	8
A + 25% Clay*	6.0	0	6.9	0	-
		.62	7.6	30	21
		1.25	8.0	62	16
		1.88	8.4	53	18
		1.25	7.4	21	21
A + 25% Clay*	4.0				
		1.88	8.1	31	24
		2.50	8.4	6	37

*A brown clay picked from one of the clay lenses on the surface of the open pit mine.

Stirrer Speed

The above series of experiments also revealed the fact that 350 rpm was insufficient speed to obtain high oil yields from sands containing low bitumen or, equivalently, high clay. Changing the apparatus to direct drive gave us capability to extract 90% of the oil from all of the tar sands tested as can be seen in Table II. Here no effort was made to maximize the yield over 90%. Where effort was made to maximize yields, it was found that, as the speed of the stirrer was increased, the yield of froth went through a maximum and declined. In Figure 1 the maximum for 8% bitumen sands occurs at 500-600 rpm and shows appreciable diminution at 800-1000 rpm. Higher grade tar sands give maximum yields at lower rpm and appear to be less sensitive to high stirrer speeds.

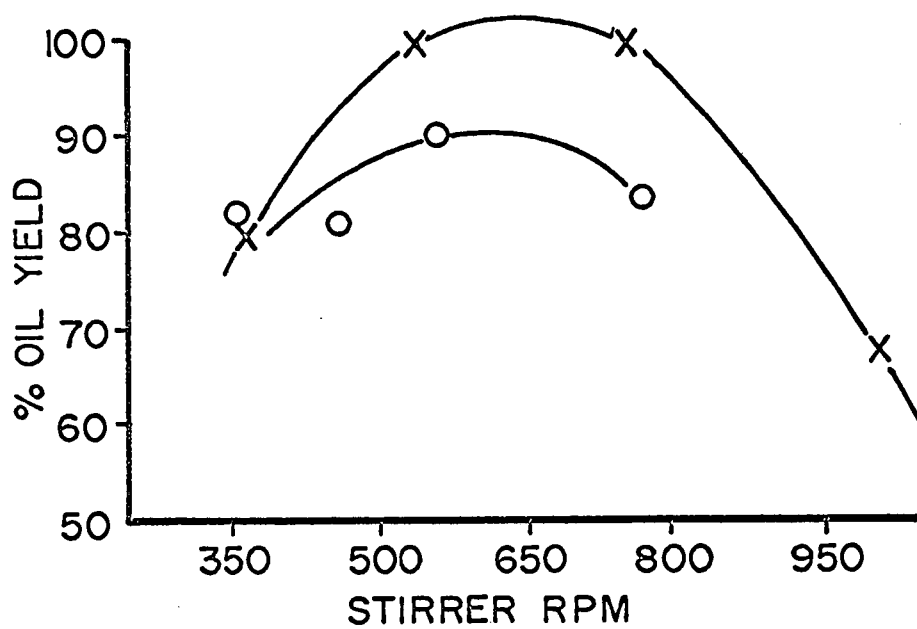
Table II

Froth Yields			
Tar Sand	% Bitumen	% Total Oil -	
		350 rpm	500 rpm
B	12.0	94	-
C	11.6	89	-
D	11.5	93	-
E	11.2	92	-
F	10.5	81, 90	-
G	9.1	84, 87, 93	-
H	8.4	81	89, 94
F + 30% Clay	7.5	80	99

Type of Impeller

Sensitivity to stirrer speed suggests also that the oil yield should be sensitive to type of agitator. Early work in the laboratories had shown that neither the Waring Blender nor ordinary laboratory impellers give good conditioning of the tar sands pulp. A study was made using flat-bladed turbine impellers made to standard specifications (7). Data from two turbines in Table III shows that this type of impeller is inferior to the U-shaped paddle stirrer. The double propeller with higher turbulence gives very low yields. Qualitatively, then, agitation causing high turbulence gives poor yields. This observation is supported by the rule of Rushton and Oldshue (8)

FIGURE 1
YIELDS VS STIRRER
SPEEDS



which states that flow rather than turbulence is favored in a process where the reaction rate increases with the ratio of impeller diameter to reactor diameter at constant power. By the formulas developed by Rushton and coworkers, the two turbines were using the same power at the speeds listed in Table III. In our process, the yield increases at least up to a diameter ratio of about 0.7 indicating a definite preference for flow rather than turbulence.

Table III

Type of Impeller
F Sands + 30% Clay, 7.5% Bitumen

<u>Impeller</u>	<u>R. p. m.</u>	<u>% Oil</u>
2-5/8" U	520	99
1-1/3" Turbine	1500	37
2-1/8" Turbine	500-700	67-62
Double Propeller	200*	18

* Run in 2" I. D. Reactor.

Other Variables

(a) Conditioning Time

Early investigations indicated that about 15 minute conditioning time was required to obtain maximum yields. Conditioning for longer times up to an hour had no effect on the yield. We standardized on 20 minutes in order to be safely out of a sensitive region. It became apparent that two events took place during the conditioning. First, the pulp was heated to 85°C. and the reagent mixed in thoroughly. Second, the hot pulp was worked into a condition enabling the oil to rise as a froth when the sands were diluted with water (flooded).

(b) Flooding

Following Clark's admonition (4), the flooding was carried out at low stirrer speeds to prevent aeration with the accompanying increase in mineral in the froth. Early tests showed that this stirring had to be continued for about 10 minutes, otherwise oil would be trapped by the sand and not allowed to float. Merely stirring the sand with a spatula would free this oil from the sand. Work by others on similar apparatus (9) has shown that high-speed stirring during flooding actually diminishes froth yield.

(c) Air Introduction

The oil which does not float contains enough mineral to be heavier than water. One way to make this oil rise to the surface is to incorporate sufficient air to give buoyancy. Therefore, improvement in yield could imply aeration. This was tested by introducing air into the bottom of the reactor under the stirrer during the conditioning stage. The U-stirrer was operated at a lower speed in order to give some chance for yield increase by air. In fact, as is seen in Table IV, the air caused less oil to froth using either the paddle or turbine stirrer. It is thought that the froth yield was lowered because the formation of the air cavities in the pulp lowered the effectiveness of the agitation.

Table IV

Air Introduction

<u>Impeller</u>	<u>R. p. m.</u>	<u>Air</u>	<u>% Yield Oil</u>
2-5/8" U	350	No	80
		Yes	72
2-1/8" Turbine	550	No	67
		Yes	49

Instability of the Pulp

During some attempts to study other variations of hot water separation, the observation was made that the froth yield from some pulps decreased if the conditioned sands were allowed to stand before flooding. After standing for five minutes, pulps from good grades of tar sands give little or no decrease in froth yields; but allowing the pulps from poorer grade sands to stand for five minutes without agitation causes a large decrease in froth yield. Furthermore, the

effect is reversible. Reagitating the pulp restores the yield. The phenomenon is examined in Table V. With this tar sand, the yield drops nearly in half after standing for five minutes but is completely restored by restirring for five minutes.

Table V

Pulp Instability
H Tar Sand, 8.4% Bitumen

<u>Conditioning Treatment</u>	<u>% Oil Yield</u>
550 rpm, 20 minutes.	89
As above, then stop for minutes	52
Stir 20 minutes, stop 5 minutes, stir 5 minutes	94

DISCUSSION

Agitation of tar sands pulp with the paddle stirrer offers a laboratory method for separating the oil from a wide range of tar sands in hot water. The procedure can be adapted to very small batch samples and requires no recycle or further treatment of any fraction. The yield can be adjusted simply by altering the stirrer speed in order to test a variable which might improve the froth yield. We are confident that high oil yields can be obtained from poor tar sands containing only 6% bitumen and perhaps even less.

A great advantage of the technique is that the critical step -- conditioning -- is isolated and can be probed to achieve an understanding of why oil floats from tar sands in hot water. The laboratory process of Clark and coworkers (4) and the Great Canadian Oil Sands pilot plant (5) have a number of potentially interrelated steps including the recycle of the water-clay phase. Proper agitation of any of the various phases could be important to froth yield. It is most convenient to be able to vary the froth yields by controlling the agitation in one known phase.

Already just by studying a few of the obvious variables in conditioning, we can outline the requirements of frothable oil. The physics of the separation requires that, in order to float, the oil must be freed of most of the mineral and must contain enough air to make the particles less dense than water. Also, the particles must be larger than 30 microns diameter in order to float in the time allowed. One observable effect of increased clay in tar sands is to make the particles of oil smaller. When the sands are not conditioned properly these flecks remain in the water-clay layer (4).

The work here shows that as the clay increases, the vigor of agitation required to condition the pulp increases. Thus, it does not seem likely that shearing oil particles into smaller fragments is an important function of conditioning. This conclusion is born out by the fact that yields are not favored by the introduction of turbulence, a high shear phenomenon. The flotation mechanism is not ordinary air flotation where particles of material cling to the face of an air bubble. Again, turbulence would be desirable for such flotation. The low shear kneading action of the agitation would favor either working mineral out of the oil or air into the oil. No choice can be made between these alternatives except to say that the existence of a rapid decay in yield with time in unagitated pulps would favor the air distribution because of superior mobility of gases over solids. Proof of this air distribution during conditioning of good grade oil sands is the subject of a report by other workers in this laboratory (9).

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